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The Sulfamic Acid Modification of the Winkler Method For Dissolved Oxygen

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According to Gordon and Cupery[1][2] the recent development of a practical process for commercial scale manufacture of sulfamic acid (NH_2HSO_3) has aroused much interest in this chemical. It has long been known that nitrites react rapidly with sulfamic acid to yield nitrogen and sulfuric acid. A novel industrial application of this reaction is the removal of excess nitrite following diazotization, for example, in dye and lake manufacture. Sulfamic acid is two to six times more effective on a weight basis than urea which is commonly used for such purposes. This ability to react with and destroy nitrites led to the authors' belief that sulfamic acid might be substituted for sodium azide as a preliminary treatment for removal of nitrites in the Winkler method for dissolved oxygen.

Properties of Sulfamic Acid.

Dry sulfamic acid is a stable, non-hygroscopic, odorless, colorless, crystalline product. It is moderately soluble in water, its solubility varying from 14.68 g. at 0° to 47.08 g. at 80°C. per 100 g. of water. Its solubility in water is decreased by presence of sulfuric acid or sodium sulfate and becomes negligible in 70-100 per cent sulfuric acid. Sulfamic acid is highly ionized in aqueous solution. The strength of the acid is indicated by its reaction with basic oxides, hydroxides and carbonates to form sulfamates. These salts are practically all soluble in water.

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Sulfamic acid is practically stable in water solution at ordinary temperature. At elevated temperatures the acid is slowly hydrolyzed to ammonium acid sulfate.(1) Salts of sulfamic acid are stable in neutral or alkaline solution, and such solutions may be evaporated to dryness on the steam bath without hydrolysis of the amido group.

In cold solution, chlorine, bromine and chlorates oxidize sulfamic acid to sulfuric acid. Potassium permanganate, chromic acid and ferric chloride exert no oxidizing action. Nitric acid yields nitrous oxide and sulfuric acid. Nitrites react rapidly with sulfamic acid, liberating nitrogen and forming sulfuric acid. This reaction may be utilized for the analytical determination of nitrites or of sulfamic acid.(3)(4)

The properties indicate that sulfamic acid might prove a desirable agent for the destruction of nitrites in the determination of dissolved oxygen and biochemical oxygen demand. It has recently been shown that the application of sodium azide is very satisfactory for this purpose in stream pollution and sewage studies.(5)(6)(7) Sulfamic acid is theoretically only two-thirds as effective as sodium azide on a weight basis as the following equations show:

$$NH_2SO_2OH\ (97) + HNO_2 \longrightarrow H_2SO_4 + N_2 + H_2O$$

$$NaN_3\ (65) + H_2SO_4 + HNO_2 \longrightarrow N_2 + H_2O + N_2O + NaHSO_4$$

However, sulfamic acid possesses the advantages of cheapness, availability, non-poisonous nature, stability in sulfuric acid and the formation of soluble sulfamates. Consequently, a comparative study of sulfamic acid and sodium azide for nitrite destruction in the dissolved oxygen determination was undertaken.

Experimental.

A comparative study of the reaction times of 2 per cent sodium azide and 4 per cent sulfamic acid solutions showed that the reaction between sodium azide and nitrites in acid solution proceeded more rapidly than the corresponding reaction with sulfamic acid. However, the latter reaction was sufficiently rapid to justify further experimental work on the use of sulfamic acid as a nitrite destroying reagent.

Tables of solubility of sulfamic acid[1] in varying concentrations of sulfuric acid show that a 20 per cent sulfuric acid solution will dissolve approximately 5 gms. sulfamic acid per 100 ml. solution at 30°C. This being true, it should be possible to add the sulfamic acid as a solution in dilute sulfuric acid in the preliminary treatment for nitrites. Accordingly, the sulfamic solutions used in all of the following experiments, unless otherwise stated, were prepared as follows:

Four grams of sulfamic acid are dissolved in 50 ml. distilled water and 50 ml. of cold 40 per cent sulfuric acid are added. In this manner very little heat is evolved, thus eliminating the possibility of hydrolysis of the amino group. The solution

thus prepared is slightly turbid but this is of no consequence. One ml. of this solution was used as preliminary treatment for destruction of nitrites in a 300 ml. dissolved oxygen sample bottle. As applied, this quantity of sulfamic acid will destroy 19.3 p.p.m. of nitrite nitrogen and is ample for all samples likely to be encountered in water and sewage work. After addition of the reagent the bottle is stoppered and shaken and then allowed to stand for ten minutes. From this point on, the procedure is identical with that of the azide modification.

Solutions of varying concentrations of nitrites in distilled water were prepared containing from 2-6 p.p.m. of nitrite nitrogen. Dissolved oxygen by the azide and the sulfamic acid modifications was then determined on this water. A similar comparison was run on sewage dilutions, trickling filter effluent, and activated sludge effluent both alone and with addition of nitrites.

Enough nitrogen was liberated in the destruction of the higher concentrations of nitrites to cause the manganese hydroxide floc to rise to the top of the bottle. However, upon reshaking the bottles in the course of dissolved oxygen determinations, the bubbles were disengaged from the precipitate, which then settled well. The results are given in Table I. The deviations in the result s obtained with these modifications vary between 0.02 and 0.10 p.p.m. and are of the same order of magnitude whether or not nitrite was added to the samples. These data demonstrate the efficacy of the use of sulfamic acid in the dissolved oxygen procedure.

A series of experiments were carried out toward the development of a shorter, simpler procedure employing sulfamic acid. It was found that the addition of sulfamic acid along with the alkaline iodide reagent (like the azide in the original Alsterberg procedure) was valueless. This is because the sodium sulfamate formed in alkaline solution does not remove nitrite and the sulfamic acid produced after the final acidification did not remove it in the presence of free iodine. It is possible to apply the sulfamic acid with the manganous sulfate solution and allow time for the nitrite removal reaction before the alkaline iodide reagent is added. This was tried employing 2 ml. of a manganous sulfate solution (480 g. of $MnSO_4 \cdot 4H_2O$ and 40 g. of sulfamic acid per liter) in a 300 ml. sample.

The data obtained in the determination of dissolved oxygen by several procedures in the presence of nitrites and copper and nitrites and organic matter are given in Table II. These data indicate that all modifications tried were satisfactory in the presence of 100 p.p.m. of copper and 14.4 p.p.m. of nitrite nitrogen. In the presence of large amounts of organic matter the nitrites were removed effectively by all modifications tried except C, employing the manganous sulfate containing sulfamic acid. This procedure definitely fails to remove nitrites satisfactorily in the presence of peptone or glucose. Although the so-called short Winkler technique was employed on these samples, the effect of oxidation of peptone and glucose during alkalinization with the subsequent reduction in the dissolved oxygen by 0.30

to 0.41 p.p.m. from the initial values in the distilled water is indicated by all satisfactory nitrite removing modifications.

Comparison of Azide and Sulfamic Acid as Preservatives for Dissolved Oxygen Samples.

In field studies of sewage treatment plants or polluted streams, it is sometimes desirable or necessary to delay the determination of dissolved oxygen for several hours after the samples have been collected. To do this it is necessary to inhibit biochemical oxidation, besides taking precautions to prevent gain or loss of oxygen due to temperature changes. It has been shown(7) that the sulfuric acid-sodium azide treatment is more effective for preserving the initial dissolved oxygen values than either sulfuric acid treatment alone or the application of the complete Winkler procedure followed by the iodine titration after the interval of storage. The efficacy of the sulfamic acid treatment for dissolved oxygen sample preservation was, therefore, compared to the sulfuric acid sodium azide treatment. The material selected for this test was a 25 per cent mixture of sewage with dilution water. This constitutes a more stringent test than is necessary for stream pollution work. Twenty-four bottles were put up, twelve of which were dosed with the azide reagents and twelve with the sulfamic acid reagent. Of these, six were used for initial D.O., three with the sulfamic acid and three with the azide treatment. The remainder were allowed to stand at room temperatures and dissolved oxygen determinations were then made on these after intervals of 2, 4 and 24 hours. Similar tests were also

made on trickling filter and activated sludge effluents. These results are shown in Table III, all titration figures being the average of three determinations.

Comparative B.O.D. Determinations by the Azide and Sulfamic Acid Methods.

In an extensive, practical, comparative study, samples from four different sources were used: The Ohio River and tributary streams in the Cincinnati area, settled sewage, an experimental trickling filter effluent, and activated sludge effluent. In all, a total of 652 duplicate samples were analyzed by the two procedures and the mean results obtained are shown in Table IV.

The individual differences between the initial dissolved oxygen results obtained by these two modifications upon all of the samples were tabulated and a frequency curve for these data is plotted in Figure 1. Positive differences signify that the azide value is greater, and negative differences that the sulfamic acid result is greater. Similar plots showing the frequency distribution of the differences in the final dissolved oxygen results and the oxygen depletion results are shown on higher levels in the same figure. It is seen that all of these curves indicate practically normal probability distribution. There may be a slight tendency for a larger frequency of negative differences in the initial dissolved oxygen data, indicating slightly higher results for the sulfamic acid modification. This tendency is not apparent in the final dissolved oxygen data.

The standard deviations obtained in each of the above sample groups and for all of the samples combined are given in Table V. These standard deviations in p.p.m. of oxygen are in general in very close agreement. There is, however, a slightly greater variation between the initial and final dissolved oxygen deviations and between the initial dissolved oxygen and oxygen depletion deviations than between the final dissolved oxygen and the oxygen depletion deviations. This is probably due to the added factor of bacterial action in oxygen consumption during the five day incubation period.

The sulfamic acid method is not recommended when the sample contains interfering substances such as suspensions of river mud, quantities of ferrous and ferric iron (50 p.p.m. or less of ferric iron does not interfere), sulfite wastes or other oxidizing and reducing agents.

SUMMARY

A modified Winkler procedure employing a solution of 4 per cent sulfamic acid in 20 per cent sulfuric acid as a preliminary treatment for the removal of nitrites in the dissolved oxygen determination has been presented.

It has been shown that this procedure is as satisfactory as the azide modification for the determination ofdissolved oxygen and biochemical oxygen demand in sewage treatment and river pollution studies.

The two modifications, azide and sulfamic acid, were compared and appear to have equal value in the prevention of biochemical

oxidation when it is necessary to store a dissolved oxygen sample for a short time.

Acknowledgment

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TABLE I.

Comparative Dissolved Oxygen Data on Water, Dilute Sewage and Treatment Plant Effluent Samples.

	Dissolved Oxygen*- P.P.M.		
	Azide Modification	Sulfamic Acid Modification	Deviation
Water + 2 p.p.m. Nitrite N	7.74	7.84	.10
Water + 4 p.p.m. Nitrite N	7.92	7.92	.00
Water + 6 p.p.m. Nitrite N	7.85	7.89	.04
10 per cent sewage	8.10	8.17	.07
10 per cent sewage + 5 p.p.m. nitrite nitrogen	7.96	8.04	.08
Activated sludge effluent	8.96	8.98	.02
Activated sludge effluent + 5 p.p.m. of nitrite nitrogen	8.78	8.88	.10
Trickling filter effluent	7.96	8.03	.07
Trickling filter effluent + 5 p.p.m. of nitrite nitrogen	7.84	7.86	.02

(*) Each value is the mean of three determinations.

TABLE II

Comparative Dissolved Oxygen Results Obtained Under Adverse Conditions with Several Azide and Sulfamic Acid Modifications

Concentration of Interfering Substances added to Distilled Water	Initial D.O. in the distilled water	D. O. Results Obtained with each modification – p.p.m.				
		A	B	C	D	E
100 p.p.m. Cu^{++} + 1.7 p.p.m. Nitrite N	7.76	7.77	7.75	7.79	7.74	7.72
100 p.p.m. Cu^{++} + 8.4 p.p.m. Nitrite N	7.76	7.75	7.75	7.88	7.76	7.80
100 p.p.m. Cu^{++} + 14.4 p.p.m. Nitrite N	7.15	7.14	7.12	7.25	7.24	7.15
1000 p.p.m. glucose + 1.7 p.p.m. Nitrite N.	7.79	7.52	7.32	7.80	7.51	7.44
1000 p.p.m. glucose + 8.4 p.p.m. Nitrite N.	7.79	7.61	7.42	10.65	7.52	7.41
500 p.p.m. peptone, no Nitrite	7.65	7.35	7.30	-	7.28	7.25
500 p.p.m. peptone + 4.8 p.p.m. Nitrite N.	7.65	7.33	7.27	-	7.30	7.31
500 p.p.m. peptone + 9.6 p.p.m. Nitrite N.	7.65	7.29	7.24	-	7.28	7.24
500 p.p.m. peptone + 14.4 p.p.m. Nitrite N.	7.65	7.30	7.25	-	7.35	7.28

A = Sulfuric acid-sodium azide preliminary treatment.
B = Sulfamic acid preliminary treatment.
C = Manganous sulfate sulfamic acid preliminary treatment.
D = Alsterberg azide treatment.
E = C and D combined.

TABLE III.

Dissolved Oxygen Results on Preservation Tests

Material	25% Sewage		10% Sewage		Activated Sludge Effluent (100%)		Trickling Filter Effluent (100%)	
Reagents Used	Azide	Sulfanic Acid	Azide	Sulfanic Acid	Azide	Sulfanic Acid	Azide	Sulfanic Acid
Initial	8.51	8.56	8.27	8.24	7.57	7.60	7.67	7.80
2-hour Interval	8.41	8.46	8.15	8.19	7.44	7.48	7.62	7.79
4-hour Interval	8.10	8.25	8.02	8.15	7.33	7.32	7.38	7.56
24-hour Interval	7.92	7.91	7.07	7.03	7.12	7.11	7.09	7.17
Loss of Dissolved Oxygen								
After 2 hrs.	0.10	0.10	0.12	0.05	0.13	0.12	0.05	0.01
After 4 hrs.	0.41	0.31	0.25	0.09	0.24	0.28	0.29	0.24
After 24 hrs.	0.59	0.65	1.20	1.21	0.45	0.49	0.58	0.63

TABLE IV

Mean Comparative Dissolved Oxygen and Oxygen Depletion Data Obtained with the Azide and Sulfamic Acid Modifications of the Winkler Method

Description of Samples	No. of Samples Compared	Dissolved Oxygen - p.p.m.				Oxygen Depletion in 5 days*	
		Initial		Final			
		Azide Modification	Sulfamic Acid Modification	Azide Modification	Sulfamic Acid Modification	Azide Modification	Sulfamic Acid Modification
Ohio River and Tributaries	322	8.80	8.80	6.53	6.54	2.25	2.26
Raw Sewage Dilutions	119	8.36	8.37	5.52	5.51	2.84	2.87
Activated Sludge Effluent Dilutions	90	8.11	8.11	6.41	6.41	1.71	1.72
Trickling Filter Effluent dilutions	121	8.27	8.28	5.50	5.45	2.78	2.81

(*) These values are multiplied by a dilution factor for each method to obtain the 5-day B.O.D.

TABLE V.

A Comparison of the Standard Deviations of the Results Obtained by the Azide and Sulfamic Acid Modifications of the Winkler Method

Description of Samples	No. of Samples in Series	Standard Deviation (p.p.m.)		
		Initial Dissolved Oxygen	Final Dissolved Oxygen	Oxygen Depletion
Ohio River and Tributaries	322	0.070	0.12	0.14
Raw Sewage Dilutions	119	0.073	0.18	0.19
Trickling Filter Effluent Dilutions	121	0.052	0.15	0.16
Activated Sludge Effluent Dilutions	90	0.047	0.15	0.16
Combined	652	0.065	0.14	0.16